UNIVERSITI TEKNOLOGI MARA

REMOVAL OF DYESTUFF FROM AQUEOUS SOLUTION USING LAYERED DOUBLE HYDROXIDE

SITI MARIAM BT SUMARI

Thesis submitted in fulfillment
requirements for the degree of
Doctor of Philosophy

Faculty of Applied Sciences

April 2016

CONFIRMATION BY PANEL OF EXAMINERS

I certify that a Panel of Examiners has met on 19th May 2014 to conduct the final examination of Siti Mariam Binti Sumari on her doctor of Philosophy thesis entitiled "Removal of Dyestuff from Aqueous Solution Using Layered Double Hydroxide" in accordance with Universiti Teknologi MARA Act 1976 (Akta 173). The Panel of examiners recommends that the student be awarded the relevant degree. The Panel of Examiners was as follows:

Rohaya Ahmad, PhD
Professor Datin
Faculty of Applied Sciences
Universiti Teknologi MARA
(Chairman)

Shariff Che brahim, PhD
Faculty of Applied Sciences
Universiti Teknologi MARA
(Internal Examiner)

Md.Pauzi Abdullah, PhD
Professor
Pusat Pengajian Sains Kimia
& Teknologi Makanan
Universiti Kebangsaan Malaysia
(External Examiner)

Nurul Wadiastuti, PhD
Institut Teknologi Surabaya
Indonesia
(External Examiner)

SITI HALIJJAH SHARIFF, PhD
Associate Professor
Dean
Institute of Graduates Studies
Universiti Teknologi MARA
Date : 6 April 2016

AUTHOR'S DECLARATION

I declare that the work in this thesis/dissertation was carried out in accordance with regulations of Universiti Teknologi MARA. It is original and is the result of my own work, unless otherwise indicated or acknowledged as referenced work. This thesis has not been submitted to other academic institution or non-academic institution for any degree or qualification.

I, hereby, acknowledge that I have been supplied with Academic Rules and Regulations for Post Graduate, Universiti Teknologi MARA, regulating the conduct of my study and research.

Name of Student	:	Siti Mariam Binti Sumari
Student I.D. No.	:	2005107028
Programme	:	Doctor of Philosophy in Science (Environment)
Faculty Thesis/Dissertation	:	Faculty of Applied Sciences
Title	:	Removal of Dyestuff from Aqueous Solution using Layered Double Hydroxide
Signature of Student	:	.....
Date	:	April 2016

ABSTRACT

Among the various techniques for colour removal, adsorption is the most efficient and practically viable. However due to the relatively high production cost and difficulty in regeneration of activated carbon conventionally used as adsorbent for dye removal, there is a need to find alternatives. Consequently, layered double hydroxide (LDH) was proposed as an alternative adsorbent. MgAl-NO_3-layered double hydroxide (LDH) (molar ratio Mg/Al: 4:1) was synthesised using coprecipitation method followed by hydrothermal treatment at 70 °C. Its calcined form (CLDH) was obtained at calcination temperature of 500 °C. The physicochemical characteristics of adsorbents, LDH and CLDH were determined prior to adsorption study involving anionic dyes (Acid Blue 29, Reactive Black 5, Reactive Orange 16 and Reactive Red 120 and a cationic dye Methylene Blue. Physical characterization using XRay diffraction, FTIR spectroscopy, scanning electron microscopy (SEM) confirmed the identity of LDH and CLDH pertaining to d_{003} position, its functional groups and morphological features. Adsorption of anionic dyes were influenced by pH, adsorbent dosage, contact time, initial dye concentration and temperature. High percentage removal for anionic dyes was favoured at pH < pH_{pzc} (9.3-10) indicating strong electrostatic interaction between negatively charged dyes and positively-charged surface of adsorbent. Complete decolorization of anionic dyes was achievable for 25 mg/L concentration within 3 hrs at 0.2 g/L LDH dosage, but higher dye concentration needed longer equilibrium time within 24 hours. Analysis of kinetic data using pseudo-first order (PFO), pseudo-second order (PSO) and intra-particle diffusion kinetic models revealed that PSO mechanism was predominant and the overall rate of dye adsorption process appeared to be controlled by more than one step. The adsorption capacity predicted by PSO ($q_{e,cal.}$) was in good agreement with that obtained experimentally ($q_{e,\ expt}$). Adsorption isotherms curves relating maximum adsorption capacity Q_o, with equilibrium concentration, *C*e have Giles's *L2*-shape suggesting strong adsorbate-adsorbent interaction. Equilibrium data modelled after Langmuir and Freundlich demonstrated good coefficient correlations (R^2 = 0.96-1.00), indicating the applicability of these isotherm models. Maximun monolayer adsorption capacity, *Q*o (mg/g) predicted by Langmuir for LDH in LDH-dye system were in the order: RB5 (229.9) >AB29 (184.4) > RO16 (172.4) > RR120. The corresponding value for CLDH were RB5 (344.8) > RR120 (303.0)> AB29 (243.9) , RO16 (243. 9) > MB (16.9). Thermodynamic parameters obtained at 298K, 308K 318K and 328K implied that adsorption of anionic dyes by LDH was exothermic, spontaneous and physical in nature with decreased disorder as a result of adsorption. CLDH displayed enhanced efficiency of dye removal and hence is suitable for higher concentration whereas LDH is suited for lesser dye concentration. The adsorption mechanism of dyes adsorption by LDH was predominantly by surface adsorption while adsorption by CLDH was predominantly via rehydration followed by ion exchange. Experiment of recyclability showed that LDH via CLDH was able to be recycled while maintaining dye uptake up to 50% in the second cycle. Expectedly in binary solutions, dye uptake experienced reduced efficiency as a result of competition for active sites by individual dyes. As a conclusion LDH and its thermal form CLDH has displayed efficiencies comparable to other adsorbents. With a possibility of regeneration, LDH is a promising adsorbent for anionic dyes and applicable too with other types of negatively charged pollutants that are present in wastewater.

TABLE OF CONTENTS